# Photo-ionization of Potassium-like Ions: Spectroscopy of Autoionizing States

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# **INTRODUCTION**

The spectroscopy of the potassium-like Ca<sup>+</sup>, Sc<sup>2+</sup>, and Ti<sup>3+</sup> ions is the goal of a series of measurements at the ALS. These ions are particularly interesting because of their transition-element character and the presence of strong configuration interaction effects on level energies and decay properties that complicate the theoretical treatment. For the production of multiply charged ions an electron-cyclotron-resonance ion source is presently being set up for the use in photon-ion interaction experiments at the ALS. As the first step in the envisaged series of measurements on ions of the potassium isoelectronic sequence, photo-ionization of singly charged Ca<sup>+</sup> was investigated in the energy range from about 20 to 50 eV. Information on photo-ionization of ground-state Ca<sup>+</sup>(3p<sup>6</sup> 4s <sup>2</sup>S) and metastable Ca<sup>+</sup>(3p<sup>6</sup> 3d <sup>2</sup>D) ions is obtained.

# **EXPERIMENT**

Beams of Ca<sup>+</sup> ions of 6 keV energy were produced using a commercial discharge ion source at the ion-beam endstation of undulator beamline No. 10.0.1. A metastable 3p<sup>6</sup> 3d <sup>2</sup>D component in the primary ion beam was found to be a few percent. This was desired for the determination of the energy and the width of the doubly excited 3p<sup>5</sup> 3d<sup>2</sup> F state that can be populated by photoexcitation of metastable Ca<sup>+</sup> ions. The ion beam was merged with a beam of 20 to 50 eV photons from the ALS. After magnetic ion charge-state separation the parent beam was collected in a Faraday cup and the Ca<sup>2+</sup> product ions were detected by a microsphere-plate detector. The photon flux was measured by a calibrated Si X-ray diode. The photon energy was scanned in steps of 5 meV for the overview spectrum at 30-meV resolution and the step size was reduced when narrower bandwidths of photon energies were employed (e.g. 0.5 meV steps for 5 meV resolution). At each photon energy, data were taken for 1 s with both beams "on" and then again for 1 s with the photon beam "off". The integrated ion current, the photon flux, and the number of product Ca<sup>2+</sup> ions collected in each 1-s phase were recorded. In one energy scan a range of typically 1 eV was covered. Numerous overlapping scans were measured to cover the total accessible energy range of interest. The alternating "beam on" and "beam off" phases allowed us to subtract the detector background which arises mainly from collisions of the parent ions with the residual gas and and from stray particles and photons produced when the ions hit surfaces. The individual energy scans were combined afterwards and a complete energy spectrum of photo-ionization of Ca<sup>+</sup> ions was obtained for the photon energy range 20 to 50 eV. The Doppler effect resulting from the counter-propagation of photons and the  $1.7 \times 10^7$  cm/s ions was corrected for. The photon energy was calibrated by an ionization-threshold measurement with K<sup>+</sup> ions (31.62 eV). The total absolute uncertainty of the present energy scale is within  $\pm 5$  meV. The present photo-ionization cross section was relative in nature. However, a previous measurement [1] by Lyon et al. using ground-state Ca<sup>+</sup>(3p<sup>6</sup> 4s <sup>2</sup>S) ions can be used to put the present results on an absolute scale. The uncertainty of this calibration is estimated to be within  $\pm 15$  %.

#### **RESULTS**

The lowest energy where sufficient photon flux was available to see photo-ionization signal was about 20 eV. This energy is well below all expected inner-shell excitation energies required for net single ionization of ground-state Ca<sup>+</sup> and even of the metastable Ca<sup>+</sup>(3p<sup>6</sup> 3d <sup>2</sup>D) ions. The energetically lowest autoionizing states are produced by photo-excitation of a 3p electron of the Ca<sup>+</sup> parent ion. The experiment shows resonant contributions of such intermediate autoionizing states only above an energy of 23.6 eV. This is in qualitative agreement with calculated energies [2,3] of resonant states which can participate in single ionization of ground-state and metastable Ca<sup>+</sup> ions with significant oscillator strengths. The peak cross section with 2.2x10<sup>-15</sup> cm<sup>2</sup> is reached at 33.19 eV with signal rates above 10<sup>5</sup> counts per second. The relatively broad resonance feature (91 meV width) is associated with 3p-photo-excitation of ground-state Ca<sup>+</sup> ions to intermediate autoionizing (3p<sup>5</sup> 3d <sup>1</sup>P) 4s <sup>2</sup>P states [2] which then decay by a Coster-Kronig transition to Ca<sup>2+</sup> plus a free electron. A comparison of the present measurement with the data of Lyon et al. is shown in Fig. 1. In the measured spectrum we also found a resonance feature with a width of as much as 0.32 eV. Since that resonance was not seen by Lyon et al., who had used a surface ion source to produce Ca<sup>+</sup> exclusively in the ground state, we attribute the peak found at 29.33 eV to  $3p\rightarrow 3d$  photo-excitation of the metastable beam component. The data are shown in Fig. 2. A theoretical prediction [3] places the dominant 3p<sup>5</sup> 3d<sup>2</sup> <sup>2</sup>F resonance at 30.1 eV. This state can decay by a super-Coster-Kronig transition and hence, a large width has to be expected. The resonance at 29.33 eV has such a large width and is therefore identified as the 3p<sup>5</sup> 3d<sup>2</sup> F resonance. Several more features in the measured spectrum are explained by the presence of metastable ions in the parent beam. Some of these features were measured with high resolution. Peak widths as narrow as 3.6 meV could be mapped out.

With the experiment extending the energy range to 50 eV and beyond it was possible to observe several complete series of Rydberg resonances associated with the photo-excitation of a 3p electron to states with high principal quantum numbers n. The series  $(3p^5 \text{ nd}^{-1}P) \text{ 4s}^{-2}P$  could be followed and resolved up to about n=23 by using the high-resolution scan mode. This series is particularly interesting since it comprises some of the most prominent resonance features in the spectrum including the enormous resonance at 33.19 eV. Even beyond the series limit of that sequence, i.e. the  $3p^5$  4s  $^1P_1$  excited state of  $Ca^{2+}$  at 42.578 eV, we find strong resonance features which we associate with photo-double-excitation of both a 3p and the 4s electron of ground-state  $Ca^+$  (for example to a  $3p^5$  nl 4p configuration). The Fano profiles observed for these resonances indicate their interference with direct (3p) inner-shell photo-ionization.

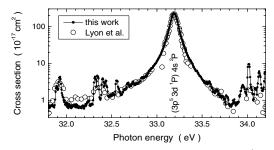


Figure 1. The dominant resonance feature in the ionization of ground-state  $Ca^+$  ions identified [2] to be associated with 3p photo-excitation of intermediate autoionizing  $(3p^5 \ 3d^{-1}P) \ 4s^{-2}P$  states. The present normalized scan data are shown along with the previous measurement of Lyon et al. [1].

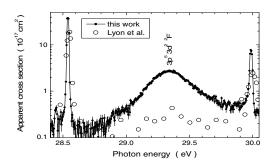


Figure 2. Measured cross section feature which we associate with the  $3p^5$   $3d^2$  <sup>2</sup>F resonance that can only be produced with significant strength by photo-excitation of metastable  $Ca^+(3p^6 \ 3d\ ^2D)$  ions. Since the metastable component of the parent ion beam is only a few percent, the real cross section maximum for this feature is around  $10^{15}$  cm<sup>2</sup>. The width of the resonance as inferred from the present data is 0.32 eV.

Future work at the ALS within this project will include photo-ionization experiments with Sc<sup>2+</sup> and Ti<sup>3+</sup> ions. The results are expected to complement photo-recombination experiments that were carried out at the heavy ion storage ring TSR in Heidelberg with Sc<sup>3+</sup> and Ti<sup>4+</sup> ions [4,5,6].

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